

## Buffer Solutions

### I. Background: Common-Ion Effect

Shift of an ionic equilibrium upon addition of a solute which contains an ion that participates in the equilibrium.

**Example:** 1.0 M HF ( $K_a = 6.6 \times 10^{-4}$ )

|             |         |   |                     |     |                                    |   |                     |
|-------------|---------|---|---------------------|-----|------------------------------------|---|---------------------|
|             | HF(aq)  | + | H <sub>2</sub> O(l) | <=> | H <sub>3</sub> O <sup>+</sup> (aq) | + | F <sup>-</sup> (aq) |
| initial     | 1.0 M   |   |                     |     | 0 M                                |   | 0 M                 |
| change      | -x      |   |                     |     | +x                                 |   | +x                  |
| equilibrium | 1.0 - x |   |                     |     | x                                  |   | x                   |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0} = x^2$$

$$\Rightarrow x = [\text{H}_3\text{O}^+] = \sqrt{K_a} = \sqrt{6.6 \times 10^{-4}} = 2.6 \times 10^{-2}$$

and approximate  $x < 5\%$  of 1.0 (better to use Harris 1% approximation) so approximation is OK. Therefore HF is 2.6% dissociated with  $\text{pH} = -\log_{10}(2.56 \times 10^{-2}) = 1.590 = 1.59$ . Remember that **when taking logarithms the number of decimal places in the result is the number of significant figures**. Here since we have two significant figures (both in 1.0 M and the value of  $K_a$ ) the pH must be reported to two decimal places.

1. Now consider the addition of enough NaF to make the solution 1 M NaF. Since



the concentration table changes

|             |         |   |                     |     |                                    |   |                     |
|-------------|---------|---|---------------------|-----|------------------------------------|---|---------------------|
|             | HF(aq)  | + | H <sub>2</sub> O(l) | <=> | H <sub>3</sub> O <sup>+</sup> (aq) | + | F <sup>-</sup> (aq) |
| initial     | 1.0 M   |   |                     |     | 0 M                                |   | 1.0 M               |
| change      | -x      |   |                     |     | +x                                 |   | +x                  |
| equilibrium | 1.0 - x |   |                     |     | x                                  |   | 1.0 + x             |

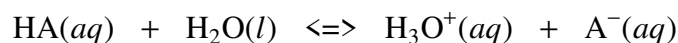
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x(1.0 + x)}{1.0 - x} \approx \frac{x(1.0)}{1.0} = x$$

$$\Rightarrow x = [\text{H}_3\text{O}^+] = K_a = 6.6 \times 10^{-4}$$

and approximate  $x < 5\%$  of 1.0 (1% better) so approximation is OK. Therefore HF is now only 0.066% dissociated with  $\text{pH} = -\log_{10}(6.6 \times 10^{-4}) = 3.180 = 3.18$

**Note:** The addition of  $\text{F}^-$  has shifted the equilibrium to the left where HF is less dissociated and a lower concentration of  $[\text{H}_3\text{O}^+]$  is present. This result is perfectly in accord with Le Châtelier's Principle. Since  $K_a$  is a constant, if  $[\text{F}^-]$  is increased then 1)  $[\text{H}_3\text{O}^+]$  must decrease and 2)  $[\text{HF}]$  increase in order to maintain the same value for  $K_a$ .

2. Problem solved with the **Henderson-Hasselbalch equation** for a weak acid dissociation



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$-\log_{10} K_a = -\log_{10} \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = -\log_{10} [\text{H}_3\text{O}^+] - \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

that is

$$\text{p}K_a = \text{pH} - \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

so

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

This equation is exact. The approximation comes in when the equilibrium concentrations are close to their initial concentrations, i.e.,

$$[\text{A}^-] \approx [\text{A}^-]_o$$

$$[\text{HA}] \approx [\text{HA}]_o$$

Then

$$\text{pH} \approx \text{p}K_a + \log_{10} \frac{[\text{A}^-]_o}{[\text{HA}]_o}$$

For the example of 1 M NaF / 1 M HF

$$[\text{F}^-] \approx [\text{F}^-]_o = 1.0 \text{ M}$$

$$[\text{HF}] \approx [\text{HF}]_o = 1.0 \text{ M}$$

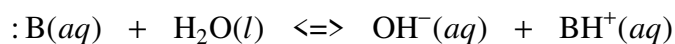
So

$$\text{pH} \approx \text{p}K_a + \log_{10} \frac{[\text{F}^-]_o}{[\text{HF}]_o}$$

$$\begin{aligned} &= -\log_{10}(6.6 \times 10^{-4}) + \log_{10} 1 \\ &= 3.18 \end{aligned}$$

This is identical to the result we obtained using the concentration table and ignoring the  $\pm x$  in comparison to 1.0 which is just approximating the equilibrium concentrations by the initial concentrations.

The Henderson-Hasselbalch equation is also applicable to the ionization of a weak base:



$$K_b = \frac{[OH^-][BH^+]}{[:B]}$$

$$-\log_{10} K_b = -\log_{10} \frac{[OH^-][BH^+]}{[:B]} = -\log_{10}[OH^-] - \log_{10} \frac{[BH^+]}{[:B]}$$

that is

$$pK_b = pOH - \log_{10} \frac{[BH^+]}{[:B]}$$

so

$$pOH = pK_b + \log_{10} \frac{[BH^+]}{[:B]}$$

This equation is exact. As with the weak acid ionization, the approximation comes in when the equilibrium concentrations are close to their initial concentrations, i.e.,

$$[BH^+] \approx [BH^+]_o$$

$$[:B] \approx [:B]_o$$

Then

$$pOH \approx pK_b + \log_{10} \frac{[BH^+]_o}{[:B]_o}$$

## II. Buffers Solved Using Concentration Tables

Many chemical reactions are sensitive to pH changes (yield and nature of products). Biochemical reactions are especially sensitive to pH (blood pH can usually only range from 7.35 - 7.45; death occurs upon prolonged exposure outside of this range. All living organisms possess naturally occurring chemical systems that minimize the effects of the addition or removal of an acid or base.

definition: **buffer** - any chemical system that can provide a resistance to pH change

examples:

1. bicarbonate:  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  (blood)
2. phosphate:  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  (intracellular fluid)

chemically:

1. weak acid and its conjugate base or
2. weak base and its conjugate acid

**Example:** 0.500 M  $\text{CH}_3\text{COOH}$   $K_a = 1.76 \times 10^{-5}$

|             |                              |   |                         |                      |                            |   |                               |
|-------------|------------------------------|---|-------------------------|----------------------|----------------------------|---|-------------------------------|
|             | $\text{CH}_3\text{COOH}(aq)$ | + | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+(aq)$ | + | $\text{CH}_3\text{COO}^-(aq)$ |
| initial     | 0.500 M                      |   |                         |                      | 0 M                        |   | 0 M                           |
| change      | -x                           |   |                         |                      | +x                         |   | +x                            |
| equilibrium | 0.500 - x                    |   |                         |                      | x                          |   | x                             |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.500 - x} \approx \frac{x^2}{0.500}$$

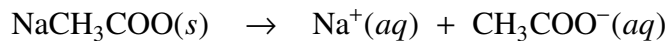
$$\Rightarrow x = [\text{H}_3\text{O}^+] = \sqrt{0.500K_a} = \sqrt{(0.500)(1.76 \times 10^{-5})} = 2.97 \times 10^{-3}$$

where  $x < 5\%$  of 0.500 (1% better) so approximation is OK. Therefore for the percentage of  $\text{CH}_3\text{COOH}$  that is ionized:

$$\frac{2.966 \times 10^{-3}}{0.500} \times 100 = 0.593\%$$

and  $\text{pH} = -\log_{10}(2.966 \times 10^{-3}) = 2.5277 = 2.528$ .

1. Now consider the addition of enough sodium acetate so the solution is 0.300 M  $\text{NaCH}_3\text{COO}$ . Since



the concentration table becomes

|             |                              |   |                         |                      |                            |   |                               |
|-------------|------------------------------|---|-------------------------|----------------------|----------------------------|---|-------------------------------|
|             | $\text{CH}_3\text{COOH}(aq)$ | + | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+(aq)$ | + | $\text{CH}_3\text{COO}^-(aq)$ |
| initial     | 0.500 M                      |   |                         |                      | 0 M                        |   | 0.300 M                       |
| change      | -x                           |   |                         |                      | +x                         |   | +x                            |
| equilibrium | 0.500 - x                    |   |                         |                      | x                          |   | 0.300 + x                     |

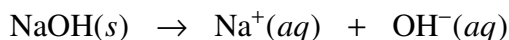
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.300 + x)}{0.500 - x} \approx \frac{x(0.300)}{0.500}$$

$$\Rightarrow x = [\text{H}_3\text{O}^+] = \frac{0.500K_a}{0.300} = \frac{(0.500)(1.76 \times 10^{-5})}{0.300} = 2.93 \times 10^{-5}$$

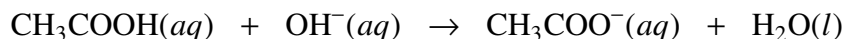
where  $x < 5\%$  (1% better) of both 0.300 and 0.500 so the approximation is OK. Therefore  $\text{CH}_3\text{COOH}$  is 0.00587% ionized with  $\text{pH} = -\log_{10}(2.933 \times 10^{-5}) = 4.5326 = 4.533$ .

**Note:** The addition of the common ion ( $\text{CH}_3\text{COO}^-$ ) has shifted the equilibrium to the left as demonstrated by the lowered percent ionization and  $[\text{H}_3\text{O}^+]$ .

2. Now to a liter of the buffer solution (#1) add 0.050 mol of NaOH



and the strong base  $\text{OH}^-$  neutralizes the undissociated acid:



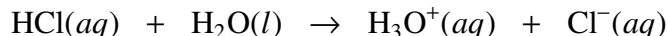
|             |                              |   |                         |                      |                            |   |                               |
|-------------|------------------------------|---|-------------------------|----------------------|----------------------------|---|-------------------------------|
|             | $\text{CH}_3\text{COOH}(aq)$ | + | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+(aq)$ | + | $\text{CH}_3\text{COO}^-(aq)$ |
| initial     | 0.500 - 0.050 M              |   |                         |                      | 0 M                        |   | 0.300 + 0.050 M               |
| change      | -x                           |   |                         |                      | +x                         |   | +x                            |
| equilibrium | 0.450 - x                    |   |                         |                      | x                          |   | 0.350 + x                     |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.350 + x)}{0.450 - x} \approx \frac{x(0.350)}{0.450}$$

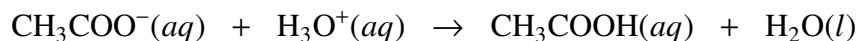
$$\Rightarrow x = [\text{H}_3\text{O}^+] = \frac{0.450K_a}{0.350} = \frac{(0.450)(1.76 \times 10^{-5})}{0.350} = 2.26 \times 10^{-5}$$

where the approximation is valid as  $x < 5\%$  (1% better) of both 0.350 and 0.450. The ionization has been reduced to 0.00453% and the pH reduced to 4.645 (compare with the 4.533 pH of the original acetic acid / sodium acetate buffer solution and the 12.70 pH of 0.050 M NaOH).

3. Now to a liter of the buffer solution (#1) add enough HCl so that it is 0.050 M HCl



and the strong acid converts the acetate ion to acetic acid:



so

|             |                              |   |                         |                      |                            |   |                               |
|-------------|------------------------------|---|-------------------------|----------------------|----------------------------|---|-------------------------------|
|             | $\text{CH}_3\text{COOH}(aq)$ | + | $\text{H}_2\text{O}(l)$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+(aq)$ | + | $\text{CH}_3\text{COO}^-(aq)$ |
| initial     | 0.500 + 0.050 M              |   |                         |                      | 0 M                        |   | 0.300 - 0.050 M               |
| change      | -x                           |   |                         |                      | +x                         |   | +x                            |
| equilibrium | 0.550 - x                    |   |                         |                      | x                          |   | 0.250 + x                     |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.250 + x)}{0.550 - x} \approx \frac{x(0.250)}{0.550}$$

$$\Rightarrow x = [\text{H}_3\text{O}^+] = \frac{0.550K_a}{0.250} = \frac{(0.550)(1.76 \times 10^{-5})}{0.250} = 3.87 \times 10^{-5}$$

where the approximation is valid as  $x < 5\%$  (1% better) of both 0.250 and 0.550 and the ionization has again been reduced, this time to 0.00774% and the pH reduced to 4.412 (compare with the 4.533 pH of the original acetic acid / sodium acetate buffer solution and the 1.30 pH of 0.050 M HCl).

**Note:** The strong base does increase the pH (4.533  $\rightarrow$  4.645) and the strong acid does decrease the pH (4.533  $\rightarrow$  4.412) but very insignificantly compared to the unbuffered solutions.

### III. Buffers Solved Using Henderson-Hasselbalch Equation

#### 1. 0.500 M $\text{CH}_3\text{COOH}$ / 0.300 M $\text{NaCH}_3\text{COO}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.300 + x)}{0.500 - x} \approx \frac{x(0.300)}{0.500}$$

This approximation states that

$$[\text{CH}_3\text{COO}^-] = 0.300 + x \approx 0.300 = [\text{CH}_3\text{COO}^-]_o$$

$$[\text{CH}_3\text{COOH}] = 0.500 - x \approx 0.500 = [\text{CH}_3\text{COOH}]_o$$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]_o}{[\text{CH}_3\text{COOH}]_o} \\ &= -\log_{10}(1.76 \times 10^{-5}) + \log_{10} \frac{0.300}{0.500} \\ &= 4.7544 + (-0.2218) = 4.5326 = 4.533 \end{aligned}$$

#### 2. 0.500 M $\text{CH}_3\text{COOH}$ / 0.300 M $\text{NaCH}_3\text{COO}$ + 0.050 M NaOH

$$[\text{CH}_3\text{COO}^-]_o = 0.300 + 0.050 = 0.350$$

$$[\text{CH}_3\text{COOH}]_o = 0.500 - 0.050 = 0.450$$

$$\begin{aligned} \text{pH} &= -\log_{10}(1.76 \times 10^{-5}) + \log_{10} \frac{0.350}{0.450} \\ &= 4.7544 + (-0.1091) = 4.6453 = 4.645 \end{aligned}$$

#### 3. 0.500 M $\text{CH}_3\text{COOH}$ / 0.300 M $\text{NaCH}_3\text{COO}$ + 0.050 M HCl

$$[\text{CH}_3\text{COO}^-]_o = 0.300 - 0.050 = 0.250$$

$$[\text{CH}_3\text{COOH}]_o = 0.500 + 0.050 = 0.550$$

$$\begin{aligned}\text{pH} &= -\log_{10}(1.76 \times 10^{-5}) + \log_{10} \frac{0.250}{0.550} \\ &= 4.7544 + (-0.3424) = 4.4120 = 4.412\end{aligned}$$

**Note:** Working with the Henderson-Hasselbalch Equation is much faster than setting up a concentration table and going through  $K_a$  to get  $[\text{H}_3\text{O}^+]$  and converting to pH **however** you should realize that both are exactly the same when we make the approximation of ignoring the change in comparison to the initial molarity, i.e., approximating the equilibrium concentrations by the initial concentrations.

#### IV. Determining New Molarities Upon Mixing Solutions

1. 100 mL 0.500 M HF + 200 mL 0.300 M NaF

$$M_1V_1 = M_2V_2 \Rightarrow M_2 = \frac{M_1V_1}{V_2}$$

$$[\text{HF}] = \frac{100(0.500)}{100 + 200} = 0.166 \text{ M}$$

$$[\text{NaF}] = \frac{200(0.300)}{100 + 200} = 0.200 \text{ M}$$

2. 0.010 mol NaF added to 300 mL solution which is 0.166 M HF and 0.200 M NaF

$$0.010 \text{ mol} / 0.300\text{L} = 0.033 \text{ M}$$

[HF] is unchanged

$$[\text{NaF}] = 0.200 + 0.033 = 0.233 \text{ M}$$